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(54) **Methods of fracturing subterranean formations**

(57) The improved recovery of hydrocarbons from subterranean formations by hydraulically fracturing a subterranean formation is accomplished. Fracturing fluids using a viscoelastic surfactant fluid containing worm-like micelles are useful to improve recovery of hydrocarbons and limit the loss of fracturing fluid into the formation fracture face. The invention further relates to novel fracturing methods useful for increasing hydrocarbon

production, limiting connate water production, resisting fracturing fluid loss into the subterranean formation, and reducing the equipment requirements in mixing and pumping fracturing fluid. The action of micelles of surfactant in aqueous zones of the subterranean formation facilitates the flowback of increased amounts of hydrocarbons once a fractured well is placed back on production.

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Description

This invention relates to the recovery of hydrocarbons from subterranean formations. More particularly, the invention relates to novel fracturing methods useful in increasing hydrocarbon production, limiting connate water production, resisting fracturing fluid loss into the subterranean formation, and reducing equipment requirements in mixing and pumping fracturing fluids.

In the recovery of hydrocarbons from subterranean formations it is common practice, particularly in formations of low permeability, to fracture the hydrocarbon-bearing formation to provide flow channels. These flow channels facilitate movement of the hydrocarbons to the wellbore so that the hydrocarbons may be pumped from the well.

In such fracturing operations, a fracturing fluid is hydraulically injected into a wellbore penetrating the subterranean formation and is forced against the formation strata by pressure. The formation strata or rock is forced to crack and fracture, and a proppant is placed in the fracture by movement of a viscous fluid containing proppant into the crack in the rock. The resulting fracture, with proppant in place, provides improved flow of the recoverable fluid, i.e., oil, gas or water, into the wellbore.

Fracturing fluids customarily comprise a thickened or gelled aqueous solution which has suspended therein "proppant" particles that are substantially insoluble in the fluids of the formation. Proppant particles carried by the fracturing fluid remain in the fracture created, thus propping open the fracture when the fracturing pressure is released and the well is put into production. Suitable proppant materials include sand, walnut shells, sintered bauxite, or similar materials. The "propped" fracture provides a larger flow channel to the wellbore through which an increased quantity of hydrocarbons can flow, thereby increasing the production rate of a well.

A problem common to many hydraulic fracturing operations is the loss of fracturing fluid into the porous matrix of the formation. Fracturing fluid loss is a major problem. Hundreds of thousands (or even millions) of gallons of fracturing fluid must be pumped down the wellbore to fracture such wells, and pumping such large quantities of fluid is very costly. The lost fluid also causes problems with the function or technique of the fracture. For example, the undesirable loss of fluid into the formation limits the fracture size and geometry which can be created during the hydraulic fracturing pressure pumping operation. Thus, the total volume of the fracture, or crack, is limited by the lost fluid volume that is lost into the rock, because such lost fluid is unavailable to apply volume and pressure to the rock face.

Hydraulic fracturing fluids usually contain a hydratable polymer which thickens the fracturing fluid when it is chemically crosslinked. Such a polymer typically is hydrated upon the surface of the ground in a batch mix operation for several hours in a mixing tank or other container, and crosslinked over a period of time to viscosify the fluid so that it is capable of carrying the proppant into the fracture. Natural polymers including polysaccharides, such as guar, have been used in this way.

One problem associated with the use of polysaccharides as viscosifiers for fracturing fluids is that the hydration and crosslinking process is time consuming and requires expensive and bulky equipment at the wellsite. Such equipment, and the associated personnel to operate it, significantly increase the cost of the fracturing operation. Further, once the polysaccharide is hydrated and crosslinked, it is not feasible to add additional polysaccharide to the solution, or to regulate the concentration of polysaccharide in the fracturing fluid in real time during the pumping of the job.

Another difficulty is that a large number of supplementary additives are required to use polysaccharides successfully, including for example: bactericides, antifoam agents, surfactants to aid dispersion, pH control agents, chemical breakers, enzymatic breakers, iron control agents, fluid stabilizers, crosslinkers, crosslinking delay additives, antioxidants, salt(s) and the like. These materials must be formulated correctly (which can be a difficult task), transported to the jobsite, and then pumped and metered accurately during the execution of the fracturing treatment.

Another disadvantage associated with such polysaccharide based fracturing fluids is that, when they are used as viscosifiers, they contain materials that concentrate in the formation during the course of the hydraulic fracturing treatment, reducing the production of hydrocarbons after the fracturing event. For example, during the course of a treatment, water from the fracturing fluid leaks into the formation leaving the polysaccharide behind. Guar concentrations in the fracture sometimes increase by as much as a factor of twenty as compared to the concentration of guar in the actual fracturing fluid.

Many fracturing fluid materials, therefore, when used in large concentrations, have relatively poor "clean-up" properties, meaning that such fluids undesirably reduce the permeability of the formation and proppant pack after fracturing the formation. Detailed studies of polysaccharide recovery in the field after hydraulic fracturing operations indicate that more than sixty percent of the total mass of polysaccharide pumped during the treatment maybe left in the fracture at the time gas or oil begins to be produced in commercial quantities. Poor clean-up is a problem.

Well productivity after fracturing increases dramatically as the amount of polysaccharide returned to the surface increases. Anything that reduces the permeability of the propped fracture to hydrocarbons is usually detrimental to the production of hydrocarbons from the well.

Other polysaccharides, such as hydroxyethylcellulose ("HEC") are sometimes believed to provide improved clean-up as compared to polysaccharide based materials; however, HEC is known to form undesirable clumps or "fish eyes"

during mixing. Further, HEC is limited to lower formation temperatures, and thus is not preferred for a wide variety of fracturing conditions.

To overcome the limitations of fracturing with natural or synthetic polysaccharides, some have suggested using relatively expensive materials as viscosity enhancers, such as viscoelastic surfactants. Fluids prepared from such materials are capable of carrying proppant into a fracture, but do not have many of the limitations of polysaccharide materials. Viscoelastic surfactants form micelles that are able to proceed into the reservoir rock, and then break up, allowing the components to be removed. Therefore, breaker materials are not customarily required, which reduces cost and improves cleanup of the fluid from the formation.

The problems encountered with viscoelastic surfactant based fluids in the past, however, include relatively large fluid losses into formations in which they have been used. Micellar-type viscoelastic fluids have not been utilized widely in fracturing treatments of relatively low permeability formations because, among other reasons, materials have not been available that would enable the maintenance of a desired viscosity at temperatures above about 130°F, which is less than the temperature at which most hydraulic fracturing operations are conducted.

Until recently, the use of such viscoelastic surfactant fluids has been restricted largely to operations in shallow, high permeability to control sand production either in conventional gravel packing operations or involving fracturing very close to the wellbore, such as in so called "frac-and-pack" type operations. The cost of viscoelastic components has rendered them too expensive, in most cases, to utilize in normal fracturing treatments of a large size and high volume.

Use of viscoelastic surfactant fracturing fluids has been limited in many cases to formations that contain clays or otherwise need soluble salts for the specific purpose of inhibiting hydration of the clay materials. If such clay materials are allowed to hydrate, problems can occur, thus the need exists for a soluble salt that can inhibit the hydration of such clay-type materials. U.S. Patent No. 5,551,516 to Norman et al. ("Norman") discloses generally fracturing stimulation of high permeability formations, and more specifically, the use of surfactant based fracturing fluids. However, Norman does not teach this invention, and in particular, application to low permeability formations. Further, Norman teaches the use of an organic activator, such as, for example sodium salicylate, which is not required in this invention.

Notably, low permeability formations present different fluid loss control challenges that typically are not addressed in fluids designed to work on high permeability formations. For example, solid fluid-loss-control additives, which are very effective in high permeability formations, have little or no utility in hydrocarbon zones of low permeability.

U.S. Patent Nos. 4,725,372 and 4,615,825 (collectively "Teot") specifically teaches and defines fluids used in treating the wellbore. This requires the use of heavy brines (e.g. greater than 12-15 lbs/gallon of brine). Heavy brines generally are not desirable in hydraulic fracturing of low permeability formations. Heavy brines can minimize fluid returns after the hydraulic fracturing treatment, adversely affecting cleanup and well productivity.

For example, fluid systems that operate effectively in ammonium chloride salts many times are frequently not compatible with much heavier calcium chloride, calcium bromide and zinc salt derived brines that typically are required for wellbore treatments. Therefore, fluids of a viscoelastic type designed for wellbore applications have not been directly useful in the past as reservoir treating fluids (sand control, acid fracturing, hydraulic fracturing, matrix acidizing, remedial scale inhibition treatments and the like) and vice-versa.

A need exists for a surfactant fluid that economically can increase hydrocarbon production, limit connate water production, resist fluid loss into the formation, and preserve the component balance of the fluid mixture. A fluid that can achieve the above while improving the precision with which fluids are delivered, and reduce equipment or operational requirements, would be highly desirable.

It has been discovered that a viscoelastic surfactant fluid may be used advantageously in many different fracturing applications to achieve results not previously believed possible using such fluids. In particular, this invention is effective in increasing hydrocarbon production following hydraulic fracturing. Further, these methods may be employed to limit connate water production after fracturing, which assists in improving the percentage of hydrocarbons recovered once a well is put back on production after fracturing.

Other advantages of the methods of this invention include that it may assist in resisting fracturing fluid loss into the subterranean formation, thereby saving money and preserving the component balance of the fracturing fluid mixture. It is also an advantage of this invention that it is possible to reduce the equipment requirements in mixing and pumping fracturing fluids at the wellsite, and improve operational efficiency in fracturing wells. This invention can be utilized to save operating expense and to improve the precision with which fluids may be delivered into the wellbore during fracturing.

In one embodiment, the invention comprises a method of reducing fluid loss into a relatively low permeability formation during fracturing by providing a viscoelastic surfactant based fracturing fluid containing wormlike micelles comprising a thickening amount of a viscoelastic surfactant comprising a surfactant ion having a hydrophobic first portion chemically bonded to an ionic hydrophilic second portion.

The fluid contains micelles, the micelles having a structure that contributes to the increased viscosity of the fluid, further wherein the wormlike micelles are capable of selectively forming, changing structure or disbanding depending

upon the polarity of the surrounding fluid in the formation.

The fluid is pumped, for example, into a relatively low permeability formation at a pressure sufficient to fracture the formation, the relatively low permeability formation having a fracture face engaged by the fluid during pumping. Typically, the formation comprises at least one largely hydrocarbon-bearing zone and at least one largely aqueous zone.

5 The viscosity of the fluid within the hydrocarbon-bearing zone is decreased, while the viscosity of the fluid within the aqueous zone is maintained. Further, the amount of viscous fluid lost into the fracture face is reduced, whereby a greater volume of viscous fluid is available for fracturing the relatively low permeability formation, and increasing the ratio of fracture size per unit volume of viscous fluid pumped into the wellbore.

10 In other methods, the invention includes enhancing the cleanup of viscoelastic surfactant based fracturing fluid from the well, or in some cases flowing back fluid from the wellbore, wherein hydrocarbon production upon flowing back fluid from the wellbore is increased.

The viscosity of fluid within at least one aqueous zone of the subterranean formation is maintained by presence of wormlike micelles in that zone of the formation, and viscosity of the fluid within at least one hydrocarbon-bearing zone is depleted by the disbanding or structural change of the micelles.

15 In many cases, the maintenance of wormlike micelles within aqueous zones contributes to an increase in hydrocarbon production from the wellbore upon flowing back fluid from the wellbore following fracturing.

In another embodiment, a method of reducing the production of water from a subterranean formation subsequent to fracturing the subterranean formation is shown. This method is directed to providing an aqueous viscoelastic surfactant based hydraulic fracturing fluid comprising an aqueous medium, an effective amount of a water soluble salt, and an effective amount of a thickener in the fluid, generating a viscous fluid comprising worm-shaped micelles; and 20 pumping the viscous fluid comprising micelles through a wellbore and into a formation at a pressure sufficient to fracture the formation. The formation may have an aqueous zone containing a significant amount of water, and a hydrocarbon zone. Micelles within the viscous fluid of the hydrocarbon zone undergo a structural change or break down, thereby decreasing the viscosity of the fluid within the hydrocarbon zone to form a thinned fluid. The thinned fluid is then 25 removed from the hydrocarbon zone of the formation. The wormlike micelles in the water zone are more stable, and a reduction in the amount of water produced from the formation during the removing step is observed. Further, the advantage of increasing the production of hydrocarbons from the subterranean formation is realized.

30 In another method, the formation is fractured by providing an aqueous viscoelastic surfactant based hydraulic fracturing fluid including a thickener comprising an aqueous medium and an effective amount of a water soluble salt, and at least one thickener. The thickener is an amine or a salt of an amine.

This method includes the steps of generating a viscous fluid comprising wormlike micelles, pumping the viscous fluid comprising such micelles through the wellbore and into the formation at a pressure sufficient to fracture the formation. The micelles enter the water zone and the hydrocarbon zone and a fracture is accomplished. The micelles 35 undergo a structural change or disband within the fluid in the hydrocarbon zone, thereby decreasing the viscosity of the fluid within the hydrocarbon zone. The well is flowed back, and hydrocarbons are produced from the subterranean formation. Significantly, there is a reduction in the amount of water produced from the subterranean formation during the removing step.

40 In one method, a procedure of fracturing a subterranean formation below the surface of the ground is disclosed using a viscous fracturing fluid that does not require prolonged hydration above the ground surface, resulting in a more efficient and less costly procedure. In this way, the fluid is prepared by simply continuously metering a concentrate at the ground surface into a blender, the concentrate comprising a thickening amount of a viscoelastic surfactant comprising a surfactant ion having a hydrophobic first portion chemically bonded to an ionic hydrophilic second portion. Further, a counter-ion having a component capable of associating with the surfactant ion and forming a viscoelastic fluid and a functionally effective amount of water are added. Mixing of the concentrate with the counter-ion and water 45 above the ground surface is performed at the blender to instantly form a viscous fracturing fluid, which is simultaneously pumped below the surface of the ground into a wellbore.

BRIEF DESCRIPTION OF THE DRAWINGS

50 Figure 1 shows a typical layout of the standard equipment used in the prior art on a large land-based fracturing job, which includes mixers to hydrate and contain the hydratable polymer;

Figure 1A illustrates the prior art methods of polysaccharide based fracturing, which includes a mixer and numerous additives, breakers, etc., needed to cause the polysaccharide to perform;

55 Figure 2 depicts a standard mixer (the particular mixer shown is Schlumberger's "Precision Continuous Mixer" or "PCM") (PCM is a trademark of Schlumberger Technology Corporation) used to hydrate polysaccharides on a well-site prior to pumping the polysaccharides to a blending unit where proppant is added prior to pumping into the

wellbore;

Figure 3 is yet another schematic representation of the flow of material in above ground equipment and into the wellbore in the prior art;

Figures 4 and 4A illustrate the flow of material that may be achieved using one invention of this application;

Figure 5 shows an illustration of the structure of a micelle of viscoelastic surfactant material as it exists intact in an aqueous environment and in disbonded form after contacting a hydrocarbon medium;

Figure 6 demonstrates how micelles exist in the water bearing formation, and remain in wormlike micellar form, thereby inhibiting water flow from the aqueous zone, while the micelles themselves degrade into smaller components and facilitate production back into the wellbore of the fluids within the hydrocarbon bearing zone; and

Figure 7 illustrates how micelles are used to assist in preventing undesirable loss of the aqueous component of the fluid into the fracture face of a relatively low permeability formation.

Figures 8, 9 and 10 shows results of tests described in Examples 9, 10 and 1 respectively, and are discussed in connection with those Examples.

Turning now to Figure 1, a fracturing configuration 9 for a land-based fracture typically includes the equipment shown. The proppant is contained in sand trailers 10 and 11. Further, water tanks 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, and 25 are shown at the top of the figure. Water is pumped from such tanks into the mixers 26 and 28. Smaller fracturing jobs would use only one such mixer. Pump trucks 27 and 29 are shown on either side of Figure 1, and they contain on their trailers the pumping equipment needed to pump the final mixed and blended slurry downhole.

Sand hopper 30 is available to receive sand from the sand trailers and distribute it into the mixers as needed. The mixers are filled with polysaccharide in a typical prior art fracturing operation, and the polymer then is hydrated using water from the water tanks. This process of hydrating the polysaccharide takes some time, and using the prior art methods that utilize guar or other hydratable polymers, the polysaccharide polymer cannot be pumped from the mixer until it is fully hydrated and ready to pump downhole. Once the polysaccharide is fully hydrated, it is no longer possible to increase viscosity by adding more polysaccharide. Should high fluid viscosity be required, the rate of polysaccharide addition from the pre-mixed slurry would be the only available means of increasing the viscosity. This would be very inefficient, however, because in many cases fluid already prepared, but of incorrect viscosity, would be discarded or unfit for use.

During fracturing, the hydrated polysaccharide is pumped from the mixers to the blenders 33 and 36, where it is blended with the proppant and then transferred to manifolds 31 and 32, respectively. The fluid containing proppant is then transferred to the pump trucks, and routed back at high pressure through treating lines 34 to rig 35, and then pumped downhole.

Figure 1A shows a typical prior art method in which water and polysaccharide are transferred from a frac tank to a mixer and then to a blender, while various additives are added along the path of the material.

Figure 2 shows a mixer 26 which comprises a slurry gel tank 37 and mixing compartments 38. The mixing compartments contain paddle blades (not shown) which are used to slowly agitate the polysaccharide to allow it to hydrate and thicken prior to addition of crosslinker and other additives and then pumping it out discharge line 39 to blending equipment. Suction line 40 carries water for mixing with the polysaccharide.

In Figure 3, the prior art methods of pumping polysaccharides hydratable are shown in which fluid from water tank 80 is mixed with polymer (or polysaccharide) 82 and pumped into precision continuous mixer 84. The next step is the relatively slow agitation and hydration of the mixture followed by addition of crosslinker and other additives to convert the polysaccharide slurry into a viscous fracturing fluid, followed by mixing with proppant 88. This resulting slurry is then transferred to the high speed blender 90 and pumped downhole at step 92.

Figures 4 and 4A show the path of material using one of the inventions disclosed herein. In Figure 4A, water 94 is mixed with viscoelastic surfactant 96 and then mixed with proppant 98 where it proceeds into a blender 100 to be pumped downhole. This process may be accomplished, for example, using a concentrate of surfactant which can be taken to a wellsite and almost immediately hydrated and blended to go downhole, without the slow agitation and slow hydration used in some prior art methods. Figure 4 shows an invention method of this invention wherein a mixer such as the PCM is not needed, but instead fracturing fluid is mixed with proppant and blended substantially at the same time that it is pumped downhole, without prolonged hydration times.

In Figure 5, a micelle of surfactant is shown in a typical configuration with hydrophilic head portions 42 and hydrophobic tail portions 43. The hydrophilic portions, when in an aqueous (polar) environment, tend to form an outer layer,

while the hydrophobic portions are directed inwards away from the aqueous environment. In the presence of sufficient amount of hydrocarbons, this wormlike micellar structure becomes unstable, reverting to a micellar structure that is not conducive to forming a viscous fluid, or to individual molecules as shown in the figure.

Figure 6 depicts a fractured subterranean formation 104 comprising an aqueous zone 110 separating a hydrocarbon zone 112. Wellbore 106 receives hydrocarbons along direction arrow 114 from the hydrocarbon zone 112. A close-up examination of the pore structure is seen for both the aqueous zone (upper) and hydrocarbon zone (lower). Sand grains 121, 122, 123, 124, 125, 108, 131, 126, 116, 127, 128, 129, 130, are shown as deposited into the formation by the fracturing fluid. Wormlike micelles 118 are seen in the space between the sand grains in the aqueous zone as a network of micelles which impede connate water flowback into the wellbore 106. The micelles within the hydrocarbon zone are dispersed into micellar subunits 120, as seen in the lower portion of Figure 6.

In Figure 7, an illustration of the benefit of micelles in controlling fluid loss is seen. Subterranean fracture 63 is shown growing outward from wellbore 64 which uses fracture fluid flow direction 75 to facilitate fracture fluid flow into the formation at 65. Fluid loss direction arrows 67-72 indicate the direction of fluid loss into the fracture face. In the case of viscoelastic surfactants, this has been found to occur by a mechanism that preserves and enhances the fracture volume.

The description and examples are presented solely for the purpose of illustrating the preferred embodiments of the invention and should not be construed as a limitation to the scope and applicability of the invention.

The invention(s) relate to novel fracturing methods useful in, among other things, increasing hydrocarbon production, limiting connate water production, resisting fracturing fluid loss into the subterranean formation, and reducing equipment requirements in mixing and pumping fracturing fluids.

The problem of excessive fluid loss has been known to detrimentally affect a well when a significant (greater than about 30%) portion of the aqueous fluid is lost into the fracture face, leaving behind the larger polymer molecules which do not diffuse into the pores of the rock. When the ratio of aqueous fluid to viscosifier is changed by such large fluid losses, problems in maintaining the integrity of the fluid occur. This is particularly a problem in relatively low permeability formations, in which large surface areas of rock fracture face are exposed to the fluid. In conventional guar based fluids, only water leaks off into the formation.

In relatively low permeability formations, e.g. less than about 10 millidarcies (hereafter "md"), where hydrocarbons are present, solid fluid-loss-control additives and fluid compositions usually show very little or no effect on fluid loss rate. Leakoff in such instances is controlled by the viscosity of the leakoff fluid. That viscosity is essentially the same as the viscosity of water for all polysaccharides because the polymer is filtered out at the surface of the rock face into which fluid loss is occurring.

It has been found that the leakoff rate of viscoelastic surfactant based fluids into similar rock is much lower than that of the polysaccharide based fluids. While this invention and its claims are not bound by any particular mechanism of operation or theory, it appears that (a) the micellar structure which provides fluid viscosity is sufficiently small so that it can move into the pore structure of the rock thereby maintaining the high viscosity of the leak off fluid and controlling total leakoff, or (b) the "equilibrium controlled" micelles break at the face of the rock producing the individual surfactant molecules which are too small to be filtered out on the rock face and therefore migrate into the pore structure of the rock where they are capable of reassembling into micelles and decreasing fluid mobility (due to regained viscosity or due to the energy required to break the micelles before the fluid viscosity can decrease and the fluid migrates deeper into the rock structure).

The use of polysaccharide fluids for hydraulic fracturing is further limited by the physical processes that control cleanup after the hydraulic fracturing treatment in low to medium permeability formations. After a hydraulic fracturing treatment the well is "tuned around", that is, the piping used during the treatment is disconnected from the wellbore, new piping is put in place to allow production of the fracturing fluids and formation fluids back to the surface through a choke at a designed flow rate. This flow rate is set based on a number of criteria including consideration of proppant back production. The total flow rate at the surface depends on the rate of flow of fluids from the fracturing treatment out of the fracture and up the wellbore, plus the rate of migration of formation fluids (hydrocarbons and connate water) into the fracture and then into the wellbore. With time, the rate of production of formation fluids, including connate water, increases until it is equal to or very nearly equal to the flow rate at the surface. At this point in time clean up of the fracture length essentially stops. Studies have shown that connate water production rate can be the limiting factor in determining guar recovery, effective fracture half length and well productivity.

The problem of excessive fluid loss has been known to detrimentally affect a well when a significant (greater than about 30%) portion of the aqueous fluid is lost into the fracture face, leaving behind the larger crosslinked polysaccharide molecules which do not diffuse into the pores of the rock. When the ratio of the aqueous fluid to viscosifier is changed by such large fluid losses, polysaccharide concentration increases by anywhere from 40 to 2000% forming pastes or rubbery semi-solids that are difficult to remove from the fracture. This limits well productivity and causes problems in maintaining the integrity of the fluid. This is particularly problematic in relatively low permeability formations, in which large surface areas of rock fracture face are exposed to the fluid. In conventional polysaccharide based fluids,

usually only water leaks off into the formation.

It has been shown by way of this invention that use of viscoelastic surfactant based fluids dramatically reduces the rate of production of connate water during the well turn-around period, thereby increasing effective fracture length and well productivity.

5 In high temperature formations, one may provide a hydraulic fracturing fluid wherein the selected thickener is erucyl methyl bis(2-hydroxyethyl) ammonium chloride. It is an object of this invention to provide a fracturing fluid with little or no residue following completion of the fracturing treatment.

The present invention comprises methods employing an aqueous viscoelastic surfactant based fracturing fluid. The fluid comprises water, a salt and a surfactant/thickener capable of forming a wormlike micelle. The fracturing fluid
10 may optionally contain a gas such as air, nitrogen or carbon dioxide to provide a foam. Optionally, it may include a cosurfactant to increase viscosity or to minimize the formation of stable emulsions which contain components of crude oil or a polysaccharide or chemically modified polysaccharide, or an organic salt or alcohol, etc.

The surfactants create fluids which have a low leakoff rate. Preferably, these fluids are insensitive to pressure. At high pressures used during a fracturing operation, little fluid is lost to the formation. This reduces the total volume of
15 fluid needed to provide the desired fracture with associated cost savings. Further, since leakoff is minimized, longer fracture length extension is obtained using micellar-type viscoelastic surfactant fluids. At low pressures, these low molecular weight surfactant systems flow out of the formation more easily with better cleanup -- showing improved well productivity after fracturing.

Viscoelastic surfactants are relatively small molecules. Each molecule is typically less than 500 grams per mole, which is less than 0.1% the size of the polymers used in some of the prior art. These small molecules will associate under certain conditions to form wormlike micelles in an equilibrium state of breaking and reforming. As dynamic structures, the micellar structure are readily altered by shear pressure, the presence of hydrocarbons, or sometimes by increased temperature. All of these features may be found in the hydrocarbon portion of the reservoir. The wormlike
20 micelles rapidly assume a structure that is not conducive to creating viscosity and/or the surfactant molecules return to their original small independent state once they are placed into the hydrocarbon bearing zone, and are no longer required to provide viscosity which is required to transport particles into the formation.

To the contrary, the molecules pumped into the aqueous zones of the formation advantageously remain behind in wormlike micellar form, and may act to block or impede the flow of water from the formation, as seen in Figure 6. The micelles of this invention are preferably wormlike in shape, as opposed to other geometric shapes such as box shaped
30 or spherical. They are spheroidal in cross-sectional area. Preferably, they are relatively long in comparison to their width, with an average aspect ratio of 100 or greater, in most cases.

Well treatment conditions allow wormlike micelles to form under surface conditions, remain stable while they are pumped down the wellbore and through the perforations into a fracture, but then undergo a structural change or disband into individual components on exposure to hydrocarbons in the reservoir rock. Cleanup is often superior to that of the
35 polymer systems, typically higher than 40%.

In addition to the viscoelastic surfactant, the aqueous fracturing fluid in accordance with the invention requires a sufficient quantity of at least one water soluble salt to effect formation stability. Typically, water soluble potassium and ammonium salts, such as potassium chloride, tetramethyl ammonium chloride and ammonium chloride are employed. Additionally, calcium chloride, calcium bromide, magnesium chloride and zinc halide salts may also be used. Other
40 useful salts include aluminum salts, zirconium salts and the like. Formation stability and in particular clay stability is achieved at a concentration level of a few percent by weight, and as such, the density of the fluid usually is not significantly altered by the presence of the salt. However, if fluid density becomes an important consideration, heavier salts may be employed.

Additional uses of the present invention may be found in acid fracturing. In acid fracturing it is desirable to pump
45 sequential stages of viscous fluids and of acids. In theory, the acid fingers into the viscous fluid. These acid fingers etch away the carbonate formation only where the formation is exposed to an acid finger. This creates a fractal type etching pattern on the rock (calcium carbonate) faces. This etched area creates flow channels for the reservoir fluids once the fracturing operation is ceased. For this process to work a mobility ratio of at least 1000 is required between the viscous fluid and the acid fluid. For guar based fluid, this requires a high guar loading and crosslinking (typically
50 with boron or zirconium) to provide the desired mobility ratio. Crosslinked polymer fluids are very similar to those used in hydraulic fracturing and suffer the same limitations as described above. In addition, the guar-based or polymer fluids simply do not work as effectively as desired. Recent laboratory results demonstrate that viscoelastic surfactant derived fluids provide superior finger generation in acid fracturing applications than conventional fluids.

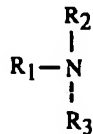
Acids are widely used to stimulate oil production from chalk reservoirs. In fracture acidizing, a fracture, or rather
55 several fractures, are first created by injecting a fracturing liquid under high pressure. After the fractures have been created, acid is injected to etch flow channels that can persist after the fractures have closed thereby increasing the productivity of the well. During some acid treatments, the acids are injected subsequent to a preflush of viscous fluid. This leads to the generation of acid fingers in the more viscous preflush and prevents the formation of near well cavities.

Studies have shown that the dissolution rate increases with increasing flow rate and increasing temperature.

Fingered acid-fracturing of vertical wells has been well studied and there are methods for analyzing fingering patterns in linear flow through fractures from vertical wells. The literature indicates that viscous fingering is a function of the mobility ratio between the fluids. Thus fluids which provide similar viscosity should perform in a similar manner. This has not been observed, however. Borate fluids tend to be too sensitive to pH to be used reliably. This is especially true at about 150-200°F. Borate fluids at initial pH of about 9 do not provide adequate fingering downhole. Zirconate fluids can be effective at high guar loadings but are difficult to remove. Under those conditions, surfactant based fluids offer superior performance and well clean-up.

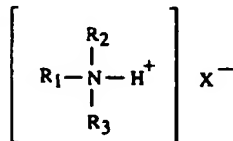
In hydraulic fracturing applications, a sufficient quantity of at least one surfactant/thickener soluble in said aqueous salt solution is employed in the method of this invention to provide sufficient viscosity to suspend proppant during placement, wherein the thickener is at least one member selected from the group consisting of:

a) an amine corresponding to the formula



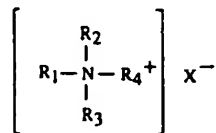
wherein R_1 is at least about a C_{16} aliphatic group which may be branched or straight chained and which may be saturated or unsaturated, R_2 and R_3 are each independently, hydrogen or a C_1 to about C_6 aliphatic group which can be branched or straight chained, saturated or unsaturated and which may be substituted with a group that renders the R_2 and/or R_3 group more hydrophilic;

b) salts of the amine corresponding to the formula



wherein R_1 , R_2 and R_3 are the same as defined hereinbefore and X^- is an inorganic anion, and;

c) a quaternary ammonium salt of the amine corresponding to the formula



wherein R_1 , R_2 , R_3 and X^- are the same as defined hereinbefore and R_4 independently constitutes a group which has previously been set forth for R_2 and R_3 , none of R_1 , R_2 , R_3 or R_4 are hydrogen, and the R_2 , R_3 and R_4 groups of the amine salt and quaternary ammonium salt may be formed into a heterocyclic 5- or 6-member ring structure which includes the nitrogen atom of the amine;

A sufficient quantity of a water soluble organic salt and/or alcohol may optionally be employed to provide desired viscoelastic properties under severe conditions. Preferably the organic salt is a water soluble carboxylate salt such as sodium or potassium salicylate or the like. However, this salt is not required in all cases. Preferably the alcohol is a cosurfactant, typically a C_4 to C_{12} aliphatic alcohol.

The thickening agent employed in the invention comprises at least one of the thickening agents set forth herein. It has been found that with certain solutions, a mixture of two or more thickeners may be preferred.

In instances where the thickening agent is an amine acid salt or a quaternary ammonium salt, the associated anion should be an inorganic anion. Preferably, X⁻ is an inorganic anion such as a sulfate, nitrate, perchlorate or halide. A halide (Cl, Br or I) is preferred, Cl and Br being most preferred.

The optional organic salt constituent of the fracturing fluid, when employed, is preferably a water soluble compound involving typically a sodium or potassium salt of an organic anion. The anion may be an aromatic organic anion such as a salicylate, naphthalene sulfonate, p- and m-chlorobenzoates, 3,5 and 3,4 and 2,4-dichlorobenzoates, t-butyl and ethyl phenate, 2,6 and 2,5-dichlorophenates, 2,4,5-trichlorophenate, 2,3,5,6-tetrachlorophenate, p-methyl phenate, m-chlorophenate, 3,5,6-trichloropicolinate, 4-amino-3,5,6-trichloropicolinate, 2,4-dichlorophenoxyacetate, toluene sulfonate, a,b-naphthols, p,p-bisphenol A or cocoamidopropyl dimethyl amine oxide. The thickening agent should be chosen such that the anion is compatible with the electrolyte present in the aqueous solution such that undesirable precipitates are not formed. Also the specific anion chosen will depend to some degree on the specific amine structure.

The thickening agent is employed in an amount which in combination with the other ingredients is sufficient to increase the viscosity of the aqueous fluid enough to maintain proppant in suspension during fluid placement. The exact quantity and specific thickener or mixture of thickeners to be employed will vary depending on the concentration of and selection of specific soluble salt(s) employed to make up the solution, the viscosity desired, the temperature of use, the pH of the solution, and other similar factors.

The concentration of the surfactant thickener can range from about 0.05 to about 6 percent by weight of the fluid. Laboratory procedures are employed to determine the optimum concentrations for any particular set of parameters. For example, when a non-protonated amine is employed as the thickener, the pH of the aqueous fluid can change to some degree the effectiveness of particular amines. More acidic solutions are required for some amines to be completely dissolved. It is possible that this fact results because the amine must become protonated before it will become effectively dissolved in the fluid.

Thickeners are selected from a group of surfactant materials capable of forming the preferable wormlike micelles as opposed to typical surfactant materials which tend to form spherical micelles or sheet-like structures. Further, in order to be useful in the present invention, the selected surfactant must be able to form the wormlike micelles over a broad range of concentrations, such as 1 to 8 percent by weight in the aqueous fluid. The number of surfactant materials that can be successfully used in the invention decreases with increasing temperature.

The preferred thickener is erucyl bis(2-hydroxyethyl) methyl ammonium chloride. Alternative thickeners may be employed either alone or in combination in accordance with the invention, including erucyl trimethyl ammonium chloride; N-methyl-N,N-bis(2-hydroxyethyl) rapeseed ammonium chloride; oleyl methyl bis(hydroxyethyl) ammonium chloride; octadecyl methyl bis(hydroxyethyl) ammonium bromide; octadecyl tris(hydroxyethyl) ammonium bromide; octadecyl dimethyl hydroxyethyl ammonium bromide; cetyl dimethyl hydroxyethyl ammonium bromide; cetyl methyl bis(hydroxyethyl) ammonium salicylate; cetyl methyl bis(hydroxyethyl) ammonium 3,4-dichlorobenzoate; cetyl tris(hydroxyethyl) ammonium iodide; bis(hydroxyethyl) soya amine; N-methyl, N-hydroxyethyl tallow amine; bis(hydroxyethyl) octadecyl amine; cosyl dimethyl hydroxyethyl ammonium bromide; cosyl methyl bis(hydroxyethyl) ammonium chloride; cosyl tris(hydroxyethyl) ammonium bromide; dicosyl dimethyl hydroxyethyl ammonium bromide; dicosyl methyl bis(hydroxyethyl) ammonium chloride; dicosyl tris(hydroxyethyl) ammonium bromide; hexadecyl ethyl bis(hydroxyethyl) ammonium chloride; hexadecyl isopropyl bis(hydroxyethyl) ammonium iodide; N,N-dihydroxypropyl hexadecyl amine, N-methyl, N-hydroxyethyl hexadecyl amine; N,N-dihydroxyethyl dihydroxypropyl oleyl amine; N,N-dihydroxypropyl soya amine; N,N-dihydroxypropyl tallow amine; N-butyl hexadecyl amine; N-hydroxyethyl octadecyl amine; N-hydroxyethyl cosyl amine; cetylamine, N-octadecyl pyridinium chloride; N-soya-N-ethyl morpholinium ethosulfate; methyl-1-oleyl amido ethyl-2-oleyl imidazolium-methyl sulfate; and methyl-1-tallow amido ethyl-2-tallow imidazolium-methyl sulfate.

To prepare the aqueous hydraulic fracturing fluid in accordance with the present invention, the thickener is added to an aqueous solution in which has been dissolved a quantity of at least one water soluble salt. Standard mixing procedures known in the art can be employed since heating of the solution and special agitation conditions are normally not necessary. Of course, if used under conditions of extreme cold such as found in Alaska or Canada, normal heating procedures should be employed.

Sometimes it is preferable to dissolve the thickener into a lower molecular weight alcohol prior to mixing it with the aqueous solution. The lower molecular weight alcohol or diol, for instance isopropanol or propylene glycol, may function to aid to solubilize the thickener. Other similar agents may also be employed. Further, a defoaming agent such as a polyglycol may be employed to prevent undesirable foaming during the preparation of the fracturing fluid if a foam is not desirable under the conditions of the treatment. If a foamed fluid is desired, a gas such as air, nitrogen, carbon dioxide or the like may be employed.

In addition to the water soluble salts and thickening agents described herein, the aqueous hydraulic fracturing fluid may contain other conventional constituents which perform specific desired functions; e.g., corrosion inhibitors, fluid-loss additives, and others as described previously herein, and the like. The proppant can then be suspended in the fracturing fluid.

EXAMPLE 1

Three 500-mL beakers were filled with 250 mL of three percent (by weight) ammonium chloride solution. Erucyl bis (2-hydroxyethyl) methyl ammonium chloride was added at three concentrations: 2%, 3% and 4% by volume. No sodium salicylate was added. The systems were stirred until all of the surfactant dissolved. Rheological measurements were performed at 110°, 130°, 150° and 175°F.

The plot of figure 10 shows the viscosity of surfactant-base fracturing fluids prepared without the addition of sodium salicylate. The data show that sufficient viscosity for adequate proppant transport ($\dot{\gamma}$ 50 cp @ 170 sec⁻¹) can be attained at fluid temperatures up to about 175°F.

EXAMPLE 2

Two 500-mL beakers were filled with 250 mL of three percent (by weight) ammonium chloride solution. Erucyl bis (2-hydroxyethyl) methyl ammonium chloride was added at 4% by volume. Sodium salicylate (0.06 wt%) was added to one beaker and 0.5 wt% erucyl amine was added to the other. The systems were stirred until all of the surfactant dissolved. Rheological measurements were performed at 175° and 200°F. The results show that erucyl amine has utility as a high temperature viscosity stabilizer.

Additive	Viscosity @ 170 sec ⁻¹ (cp)	
	175°F	200°F
sodium salicylate (0.06 wt%)	108	21
erucyl amine (0.5 wt%)	136	81

EXAMPLE 3

Two 500-mL beakers were filled with 250 mL of three percent (by weight) ammonium chloride solution. Erucyl bis (2-hydroxyethyl) methyl ammonium chloride was added at 4% by volume. Cocoamidopropyl dimethyl amine oxide (0.6 wt%) was added to one beaker. The systems were stirred until all of the surfactant dissolved. Rheological measurements were performed at 130°, 150° and 175°F.

The results show that cocoamidopropyl dimethyl amine oxide (0.6 wt%) has utility as a viscosity enhancer in this temperature range.

Additive	Viscosity @ 170 sec ⁻¹ (cp)		
	130°F	150°F	175°F
none	213	198	174
cocoamidopropyl dimethyl amine oxide (0.6 wt%)	306	210	195

EXAMPLE 4

Example 4 demonstrates properties which may be obtained using different viscosifying agents (benzoic acid derivatives). To a 3% ammonium chloride solution in a Waring blender, the following were dissolved: 0.5 mM benzoic acid derivatives like, sodium salicylate, 3-hydroxy benzoic acid, 4- and 5-methyl salicylic acid. The solution was mixed well and deaerated before measuring the viscosity on a reciprocating capillary viscometer. The viscosity was measured at various temperature from 80 F to 225 F). The viscosity values at 200 degrees F are provided below:

Substituted benzoic acid (Na salt)	% erucyl bis (2-hydroxyethyl) methyl ammonium chloride	Viscosity @ 100 S ⁻¹ (200 F)
2-hydroxy benzoic acid	4	88
4- hydroxy benzoic acid	4	44
Amino-2-hydroxy benzoic acid	4	68
3,5-Dinitro-2-hydroxy benzoic acid	4	73
5-Methyl-2-hydroxy benzoic acid	4	100

(continued)

Substituted benzoic acid (Na salt)	% erucyl bis (2-hydroxyethyl) methyl ammonium chloride	Viscosity @ 100 S ⁻¹ (200 F)
5-Methyl-2-hydroxy benzoic acid	5	120
4-Methyl-2-hydroxy benzoic acid	4	91
3,5-Di-isopropyl-2-hydroxy benzoic acid	4	75

4-and 5-substituted 2-hydroxy benzoic acid gave sufficient viscosity (57 sec⁻¹) even at 220 F at a Erucyl bis (2-hydroxyethyl) methyl ammonium chloride concentration of 4%.

EXAMPLE 5**Experiments in the Presence of Polysaccharide (guar)**

In a similar experiment, to 3% ammonium chloride solution, dissolve 0.5 mM sodium salicylate. To this hydrated guar is added to get a final concentration of 2 to 5 lb/1000 Gal followed by 0.5 to 5% surfactant solution. The solution is mixed well and viscosity is measured on a reciprocating capillary viscometer. The viscosity of 5% Erucyl bis (2-hydroxyethyl) methyl ammonium chloride in the presence of 5 lb Guar is given below:

	n'	k'	Temp (F)	Viscosity @ 100 S ⁻¹
1	0.3942	0.2075	90	610
2	0.2230	0.1960	150	262
3	0.3221	0.0957	175	202
4	.4772	0.0091	200	40

EXAMPLE 6

Example 6 provides for the addition of fluoro compounds and cosurfactants to prevent emulsions. The presence of fluoro compounds and other non-ionic surfactants as co-surfactants with Erucyl bis (2-hydroxyethyl) methyl ammonium chloride are examined. They are found to be useful as deemulsifiers in Erucyl bis (2-hydroxyethyl) methyl ammonium chloride-diesel systems. Addition of 0.001% to .1% Fluorad-FC 750 and Fluorad FC 754; and non-ionic and cationic surfactant blends were found to decrease the formation of emulsion. The de-emulsification was tested by two methods. To 10 ml of Erucyl bis (2-hydroxyethyl) methyl ammonium chloride gel, 1 μ l to 200 μ l of the de-emulsifier was added and swirled well. To this 20 ml of diesel is added and shaken well for 30 seconds. The efficiency of different surfactants were compared from the time required to separate it into two layers. It is also tested by looking at the pressure required to filter the mixture through a Whitmann membrane. The presence of flour-compounds and other surfactants made the filtration easier.

The viscosity of erucyl bis (2-hydroxyethyl) methyl ammonium chloride in the presence of these compounds were also tested and it is shown that these compounds enhance viscosity of Erucyl bis (2-hydroxyethyl) methyl ammonium chloride.

EXAMPLE 7

A series of experiments was conducted to determine the half lives of viscoelastic surfactant-base foams generated at elevated temperature and pressure. The results show adequate foam stability up to 190°F.

The apparatus uses a heated 250-mL ISCO syringe pump to feed the liquid phase into a foam generator. A nitrogen bottle with a Brooks digital flow controller feeds the gas into the foam generator. The foam passes by a sight glass that allows one to observe the foam texture and bubble size distribution, then goes on to fill a collection vessel with a glass wall. The cell is heated by a water circulating from a Hakke bath. An outlet is fitted on the collection vessel that allows foam sampling.

One liter of a base fluid composed of 4 vol% erucyl bis (2-hydroxyethyl) methyl ammonium chloride + 0.06 wt% sodium salicylate was prepared in the manner described in previous examples. The foams were generated at about 1100 psi, then pumped into the preheated collection vessel. The half lives of foams (the time at which 50% of the base

fluid has separated from the foam) were measured at four test temperatures: 150°, 175°, 185° and 190°F. The results are shown in the following table.

Temperature (°F)	Half Life (hr)
150	>6
175	3
185	2.5
190	0.6

The results show adequate foam stability up to 190°F.

EXAMPLE 8A

The fluid leakoff control characteristics of surfactant based fluids to polymer based fluids was evaluated in dynamic fluid loss tests. This test procedure simulates the leakoff of fracturing fluids into a porous media under representative hydraulic fracturing conditions. The tests were conducted with a generic Borate-crosslinked guar fracturing fluid and a generic surfactant base fluid, the additives and their concentration as specified in Table 1. The tests involve maintaining a 1000 psi differential pressure across the length of the core, for a period sufficiently long enough so that a steady leakoff rate is established. Steady leakoff conditions are established either when an impermeable external filter cake forms on the face of the core, or when the internal pores are filled with an internal filter cake. Steady leakoff rate can also exist when the leakoff control mechanism is viscosity controlled.

Table 1: Composition of test fluids

<u>A</u>		<u>B</u>	
<u>Name</u>	<u>Concentration</u>	<u>Name</u>	<u>Concentration</u>
Guar	20 lb/1000 gal	Ammonium Chloride	250 lb/1000 gal
KCl	167 lb/1000 gal	Sodium Salicylate	5 lb/1000 gal
Antifoam	0.5 gal/1000 gal	**	40 gal/1000 gal
Bactericide	0.25 gal/1000gal	**Composition comprised of 75% erucyl methyl bis(2-hydroxyethyl) ammonium chloride, and 25% isopropyl alcohol	
Xlinker	1.5 lb/1000 gal		
Xlinker activator	7 gal/1000 gal		
Surfactant	1 gal/1000 gal		
Diesel No. 2	20 lb/1000 gal		

The retained permeability of the cores after leakoff was estimated from the pressure drop required to flow brine at a constant flow rate through the core. The direction of the flow is reversed in comparison to the direction of leakoff, so that the flow back retained permeability is representative of the permeability to the flow of formation fluid.

EXAMPLE 8B

Table 2 shows results obtained as in 8B further in that it shows the results of the dynamic fluid loss tests for the guar based fluid and our surfactant based fluid along with the matrix retained permeability after 25 min. during flow back. These data demonstrate that the surfactant fluid has better leakoff control characteristics. The data further dem-

onstrate that, in comparison to polymer based fluids, the reduction in retained perm with the surfactant based fluid for brine (formation water) is not only lower but also more sustainabl . This demonstrates that in comparison to polysaccharide based fluids, the surfactant fluid would delay the entry of formation water into the fracture, thus enhancing the fracture cleanup potential.

Table 2:

Comparison of the leakoff characteristics of a Polymer based fluid and a Viscoelastic Surfactant fluid				
Example	Fluid	Leakoff (ml)		Retained Perm after 25 min
		1 min	50 min	
A	20 lb/1000 gal Borate XL Guar	1.2	12.9	40.0%
B	4% mixture:***	1.3	5.8	8.2%

***Composition comprised of 75% erucyl methyl bis(2-hydroxyethyl) ammonium chloride, and 25% isopropyl alcohol

EXAMPLE 9

The case history as seen in Figure 8 shows the results from three treatments that were performed on gas wells. The formation permeability was approximately 25 mD. The well operator had indicated, based on previous experience in the area, what the expected production rates were for these wells. For each well, when the formation was fractured with the surfactant-base fracturing fluid of this invention. The resulting production rate was significantly higher than expected.

EXAMPLE 10

The case history of Figure 9 shows the results of treatment of three zones in a gas well with a viscoelastic surfactant-base fracturing fluid. The production rates from each zone are compared with those from an offset well that had been fractured with a polysaccharide-based fluid (guar). An production-rate improvement ranging from 27% to 73% was observed when the surfactant-base fracturing fluid was used.

EXAMPLE 11

Examples were prepared with different viscosifying agents (benzoic acid derivatives), and they showed the results below. To a 3% ammonium chloride solution in a Waring blender, dissolve 0.5 mM benzoic acid derivatives like, sodium salicylate, 3-hydroxy benzoic acid, 4- and 5-methyl salicylic acid. The solution is mixed well and de-aerated before measuring the viscosity on a reciprocating capillary viscometer. The viscosity was measured at various temperature from 80 F to 225 F). The viscosity at 200 F is given in Table 3.

Table 3 -

Examples Using Various Viscosifying Agents		
Substituted benzoic acid (Na salt)	% erucyl bis (2-hydroxyethyl) methyl ammonium chloride	Viscosity @ 100 S ⁻¹ (200 F)
2-hydroxy benzoic acid	4	88
4- hydroxy benzoic acid	4	44
Amino-2-hydroxy benzoic acid	4	68
3,5-Dinitro-2-hydroxy benzoic acid	4	73
5-Methyl-2-hydroxy benzoic acid	4	100
5-Methyl-2-hydroxy benzoic acid	5	120
4-Methyl-2-hydroxy benzoic acid	4	91
3,5-Di-isopropyl-2-hydroxy benzoic acid	4	75

Four and 5-substituted 2-hydroxy benzoic acid gave sufficient viscosity (57 sec⁻¹) even at 220 F at a erucyl bis (2-hydroxyethyl) methyl ammonium chloride concentration of 4%.

EXAMPLE 12

Experiments in the presence of polysaccharides. (guar polymers). In a similar experiment, to 3% ammonium chloride solution, dissolve 0.5 mM sodium salicylate. To this hydrated guar is added to get a final concentration of 2 to 5 lb/1000 Gal followed by 0.5 to 5% surfactant solution. The solution is mixed well and viscosity is measured on a reciprocating capillary viscometer. The viscosity of 5% erucyl bis (2-hydroxyethyl) methyl ammonium chloride in the presence of 5 lb Guar is given below.

	n'	k'	Temp (F)	Viscosity @ 100 S ⁻¹
1	0.3942	0.2075	90	610
2	0.2230	0.1960	150	262
3	0.3221	0.0957	175	202
4	.4772	0.0091	200	40

The following addresses the issue of addition of fluoro compounds and to prevent emulsion, i.e. fluoro compounds and co-surfactants:

The presence of fluoro compounds and other non-ionic surfactants as co-surfactants with Erucyl bis (2-hydroxyethyl) methyl ammonium chloride are examined. They are found to be useful as deemulsifiers in Erucyl bis (2-hydroxyethyl) methyl ammonium chloride-diesel systems. Addition of 0.001% to .1% Fluorad-FC 750 and Fluorad FC 754; and non-ionic and cationic surfactant blends were found to decrease the formation of emulsion

The de-emulsification was tested by two methods. To 10 ml of erucyl bis (2-hydroxyethyl) methyl ammonium chloride gel, 1 ul to 200 ul of the de-emulsifier was added and swirled well. To this 20 ml of diesel is added and shaken well for 30 seconds. The efficiency of different surfactants were compared from the time required to separate it into two layers. It is also tested by looking at the pressure required to filter the mixture through a Whitmann membrane. The presence of flour-compounds and other surfactants made the filtration easier.

The viscosity of erucyl bis (2-hydroxyethyl) methyl ammonium chloride in the presence of these compounds were also tested and it is shown that these compounds enhance viscosity of erucyl bis (2-hydroxyethyl) methyl ammonium chloride.

The invention has been described in the more limited aspects of preferred embodiments hereof, including numerous examples. Other embodiments have been suggested and still others may occur to those skilled in the art upon a reading and understanding of the this specification. It is intended that all such embodiments be included within the scope of this invention.

EXAMPLE 13

Blending tests were performed with the Witco surfactant containing erucyl methyl bis(2-hydroxyethyl) ammonium chloride, available from the Witco Chemical Company (hereafter in this example set forth as "SURFACTANT").

The tests showed the invention of this application may be successfully utilized by pumping the surfactant directly to the blender, without prolonged hydration in a mixer as required in the prior art fracturing methods. Thus, it will be possible to achieve viscosity increases and almost simultaneously pump the fracturing fluid into the wellbore, avoiding the use of an extra mixing or hydration step, thereby saving substantial time and resources, and facilitating real time adjustment of viscosity levels.

For example, SURFACTANT has no problem yielding its viscosity in either continuous or batch mix techniques using existing equipment and methods set up on the frac boats. Metering was accomplished using a combination of 75% of erucyl compound and 25% of isopropyl alcohol.

The same continuous mix equipment set up used for PermFRAC™ treatments were arranged and performed with the ClearFRAC™ material mix test. The SURFACTANT was placed in a returnable tote on the second floor mixing deck of an offshore fracturing boat, next to the skid. The tote was rolled just prior to use by using; the product being taken off bottom and pumped back on top. The 3% NH₄Cl was cut into 230 bbls of city fresh water located in the starboard 3 below deck boat tank. Water temp was 88 degrees F. No high temp stabilizer was put in the mix water, simulating worst continuous mix conditions

Two skid pumps (0 to 40 bpm) were primed and plumbed into the suction manifold of the starboard blender. The starboard in-line was the pump used. Prior to pumping 3% NH₄Cl the blender and pump were first lined out using river water. The pump rate was set at 15 bpm (barrels per minute). The surfactant was set at 25 gpm (gallons per minute) using one of the pumps (4% surfactant loading). Once the test was started samples were taken at the discharge

manifold of the blender, at the suction of the triplex pump, and down stream of the triplex pump. A total of 8 samples were taken, 4 at the blender, and 2 each from the suction and downstream sides of the triplex. A total of 60 bbls of clean fluid was mixed followed by 50 bbls of slurried fluid ramped from 1 to 15 ppa using 12/20 proppant.

5 **Continuous Blend Test Results**

Table 4 lists the Fann 35 measurements taken on the collected samples. The data shows the SURFACTANT was fully yielded coming out of the blender, indicating enough shear is imparted to the surfactant in the blender slinger to fully yield the product - no additional time or shear is required. No sand accumulation problem was seen when the hoses and equipment were inspected after the mix test. The only problem encountered was the one inch hose feeding the surfactant to the blender was taxed to deliver the SURFACTANT material at 25 gpm, even though an A pump was used. A two inch line is recommended. Also, the 550 gallon tote appears to be a good working tank to pull from for continuous mix. The 550 gal tote placed on a 110 gal tote (i.e. placed ~3 feet high for additional hydrostatics) is therefore recommended as preferred.

15 **Batch Mix Test Conditions**

A total of 25 bbls of 4% SURFACTANT was batch mixed in 3% NH₄Cl using one of the deck 50 bbl paddle tank blenders. No centrifugal pump was used. The paddle was set at medium speed (~30-40 rpm). Water temp was 88 F. The SURFACTANT was fed into the fluid from the top at a rate of ~6 gpm.

20 **Batch Mix Test Results**

During the blending test it was noticed that the SURFACTANT started to yield viscosity before all of the material was added (within 3 minutes of initial addition). It took a total of ~7 minutes to add the SURFACTANT material.

The last portion of SURFACTANT had no problem shearing into the viscosified fluid. Fann 35 measurements showed the SURFACTANT was fully yielded within 10 minutes after the last portion of SURFACTANT was added. The test showed that even at medium paddle speed plenty of shear is available to shear in and readily yield the SURFACTANT product.

30 **Conclusion As To Example 13 Test Data**

The continuous mix test showed the SURFACTANT ClearFRAC™ material was fully yielded coming out of the discharge of the blender, showing the blender delivers an ample amount of shear to yield the product. For this mix test the ambient temperature of the SURFACTANT and mix water were in the upper 80's. The effects of lower temperature mix water and surfactant on how well the blender will yield the SURFACTANT product is not known at this time.

The batch mix test performed showed that the SURFACTANT material can be easily batch mixed. A moderate amount of shear will readily yield the SURFACTANT material. To mix below deck the smaller 230 and 250 bbl tanks are recommended over the larger 500 and 550 bbl tanks, with the tanks no more than 95% full to enhance fluid circulation.

Table 4 :

ClearFRAC Mix Test On BO30 Using 4% Witco Surfactant in 3% NH ₄ Cl		
Fluid	Temp	170 sec-1
Lab Sample	85 F	156
	150 F	135
Batch Mix Sample	88 F	162
	150 F	141
POD 1 minute	87 F	150
	150 F	132
POD 2 minute	87 F	165
	150 F	138
POD 3 minute	87 F	174
	150 F	144

Table 4 : (continued)

ClearFRAC Mix Test On BO30 Using 4% Witco Surfactant in 3% NH ₄ Cl		
Fluid	Temp	170 sec-1
POD 4 minute	87 F	180
	150 F	147
Triplex Suction 2 minute	87 F	159
	150 F	135
Triplex Suction 4 minute	87 F	180
	150 F	147
Downstream of Triplex 2 minute	87 F	156
	150 F	135
Downstream of Triplex 4 minute	87 F	174
	150 F	140

Claims

1. A method of reducing fluid loss into a relatively low permeability formation during fracturing of the formation, comprising:

a) providing a viscoelastic surfactant based fracturing fluid having

- i) a thickening amount of a surfactant capable of forming wormlike micelles, and
- ii) an aqueous medium;

b) generating a viscous fluid comprising wormlike micelles, the micelles having an elongated structure, the micelles being capable of supporting an increased viscosity of the fluid, further wherein the micelles are capable of selectively forming or disbanding based upon the polarity of the surrounding fluid in the formation;

c) pumping the viscous fluid comprising wormlike micelles through a wellbore and into a formation at a pressure sufficient to fracture the formation, the formation having a fracture face engaged by the fluid, further wherein the formation comprises at least one largely hydrocarbon-bearing zone;

d) reducing the loss of viscous fluid into the fracture face; and

e) thereby increasing the volume of viscous fluid available for fracturing the formation, and increasing the ratio of fracture volume per barrel of viscous fluid pumped into the wellbore.

2. A method of reducing the production of connate water from a subterranean formation subsequent to fracturing the formation, comprising:

a) providing an aqueous viscoelastic surfactant based hydraulic fracturing fluid comprising

- i) an aqueous medium,
- ii) an effective amount of a water soluble salt, and
- iii) an effective amount of a thickener,

b) generating a viscous fluid comprising micelles, the micelles having hydrophobic and hydrophilic portions;

c) pumping the viscous fluid comprising wormlike micelles through a wellbore and into a formation at a pressure sufficient to fracture the formation, the formation having an aqueous zone containing connate water and a hydrocarbon zone;

d) admitting micelles into the aqueous zone;

e) facilitating the breakdown of micelles within the hydrocarbon zone, thereby decreasing the viscosity of the fluid within the hydrocarbon zone to form a thinned fluid;

f) removing thinned fluid from the hydrocarbon zone of the formation; and

g) reducing the amount of connate water produced from the formation during the removing step.

3. A method of fracturing a subterranean formation comprising:

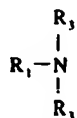
a) providing an aqueous viscoelastic surfactant based hydraulic fracturing fluid including a thickener comprising:

i) an aqueous medium;

ii) an effective amount of an inorganic water soluble salt,

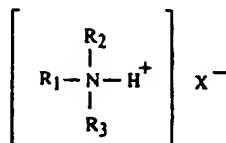
iii) an effective amount of at least one thickener in the fluid, the thickener being at least one member selected from the group consisting of

a) an amine corresponding to the formula



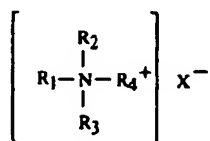
wherein R₁ is at least about a C16 aliphatic group which may be branched or straight chained and which may be saturated or unsaturated, R₂ and R₃ are each independently, hydrogen or a C1 to about C6 aliphatic group which can be branched or straight chained, saturated or unsaturated and which may be substituted with a group that renders the R₂ or R₃ group more hydrophilic, or

b) salts of the amine corresponding to the formula



wherein R₁, R₂ and R₃ are the same as defined herein and X⁻ is an inorganic anion, or

c) a quaternary ammonium salt of the amine corresponding to the formula



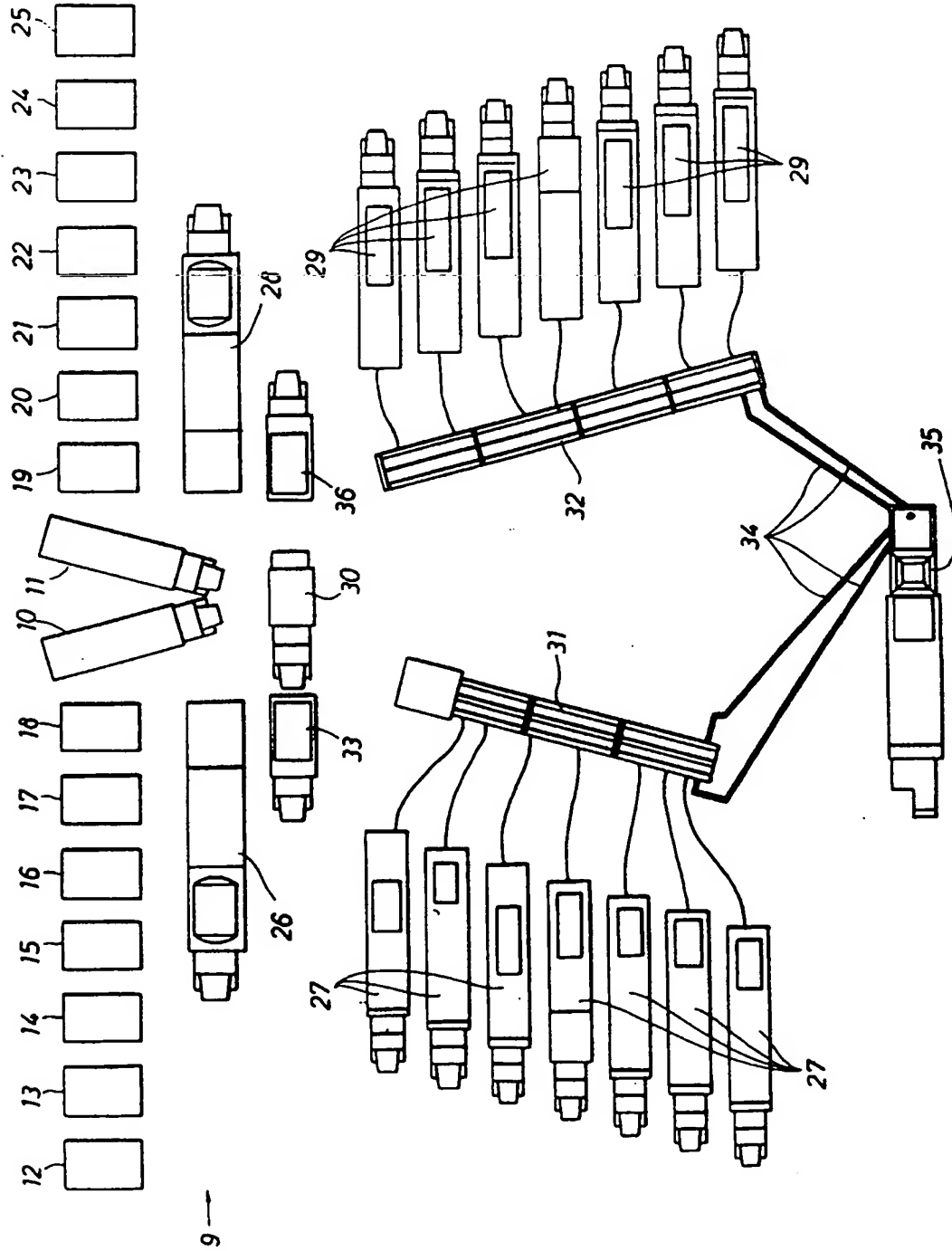
wherein R₁, R₂, R₃ and X⁻ are the same as defined herein and R₄ constitutes a group which has previously been set forth for R₂ and R₃, none of R₁, R₂, R₃ or R₄ are hydrogen, and the R₂, R₃ and R₄ groups of the amine salt and quaternary ammonium salt may be formed into a heterocyclic 5- or 6-member ring structure which includes the nitrogen atom of the amine;

b) generating a viscous fluid comprising micelles;

c) pumping the viscous fluid comprising micelles through a wellbore and into a formation at a pressure sufficient to fracture the formation, the formation having an aqueous zone and a hydrocarbon zone, the aqueous zone comprising water;

- d) facilitating entry of micelles into the aqueous zone;
 - e) structurally altering the micelles within the fluid in the hydrocarbon zone, thereby increasing the viscosity of the fluid within the hydrocarbon zone;
 - 5 f) removing fluid from the hydrocarbon zone;
 - g) producing hydrocarbons from the subterranean formation; and
 - 10 h) reducing the amount of water produced from the subterranean formation during the removing step
4. A method of fracturing a subterranean formation below the surface of the ground using a viscous fracturing fluid without prolonged hydration of the fracturing fluid above the ground surface, comprising:
- 15 a) providing a concentrate at the ground surface, the concentrate comprising a thickening amount of a surfactant capable of forming wormlike micelles;
 - b) providing an aqueous fluid component;
 - c) providing a water soluble salt;
 - 20 d) mixing the concentrate with the aqueous fluid component and water soluble salt above the ground surface to form a viscous fracturing fluid while substantially simultaneously pumping the viscous fracturing fluid below the surface of the ground into a wellbore.
5. The method of claim 4 further comprising the step of:
- 25 d) pumping the viscous fracturing fluid into the formation at a pressure sufficient to fracture the formation, wherein the formation is fractured at its fracture face
6. The method of claim 5 wherein the formation comprises a hydro-carbon bearing zone and an aqueous zone, further comprising the steps of:
- 30 e) facilitating a decrease in viscosity of the viscous fracturing fluid within a hydrocarbon-bearing zone; and
 - f) maintaining the viscosity of the viscous fluid within an aqueous zone.
7. The method of claim 6 further comprising the steps
- 35 g) reducing loss of viscous fracturing fluid into the fracture face; and
 - h) thereby increasing the volume of viscous fluid available for fracturing the formation, and increasing the ratio of fracture size per unit volume of viscous fracturing fluid pumped into the wellbore.
8. A method of fracturing a subterranean formation using a viscous fracturing fluid, comprising:
- 40 a) providing a concentrate at the ground surface, the concentrate comprising an effective amount of a thickener,
 - b) providing an aqueous fluid component;
 - 45 c) blending the concentrate with the aqueous fluid component to form a viscous fracturing fluid while pumping the viscous fracturing fluid below the surface of the ground into a wellbore without prolonged hydration.
9. The method of claim 8 further comprising the step of:
- 50 d) pumping the viscous fracturing fluid into the formation at a pressure sufficient to fracture the formation, wherein the formation is fractured at its fracture face
10. The method of claim 9 further comprising the steps of:
- 55 e) facilitating a decrease in viscosity of the viscous fracturing fluid within a hydrocarbon-bearing zone; and
 - f) maintaining the viscosity of the viscous fluid within an aqueous zone.

FIG. 1



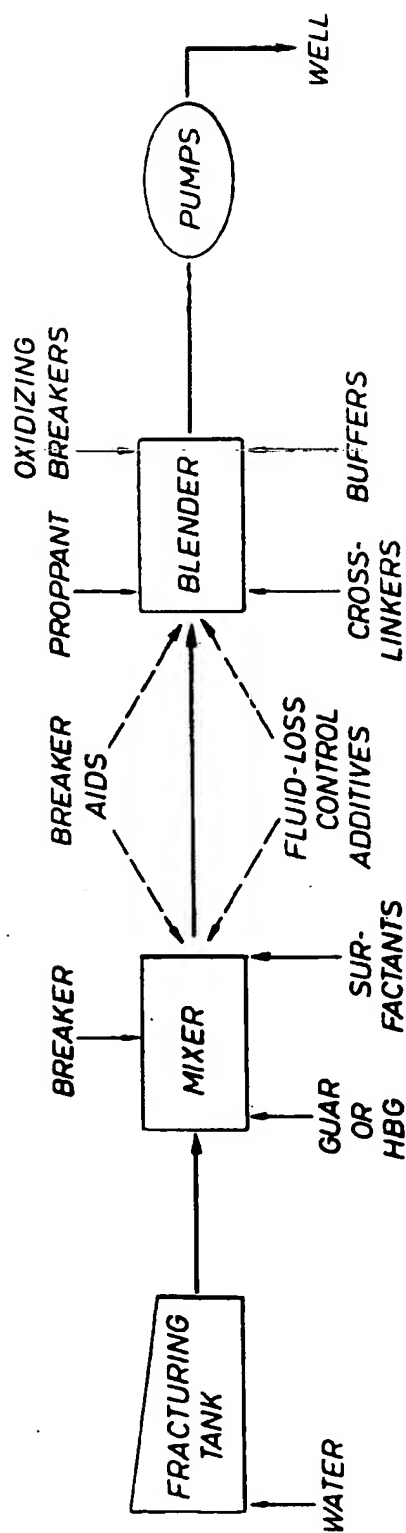


FIG. 1A

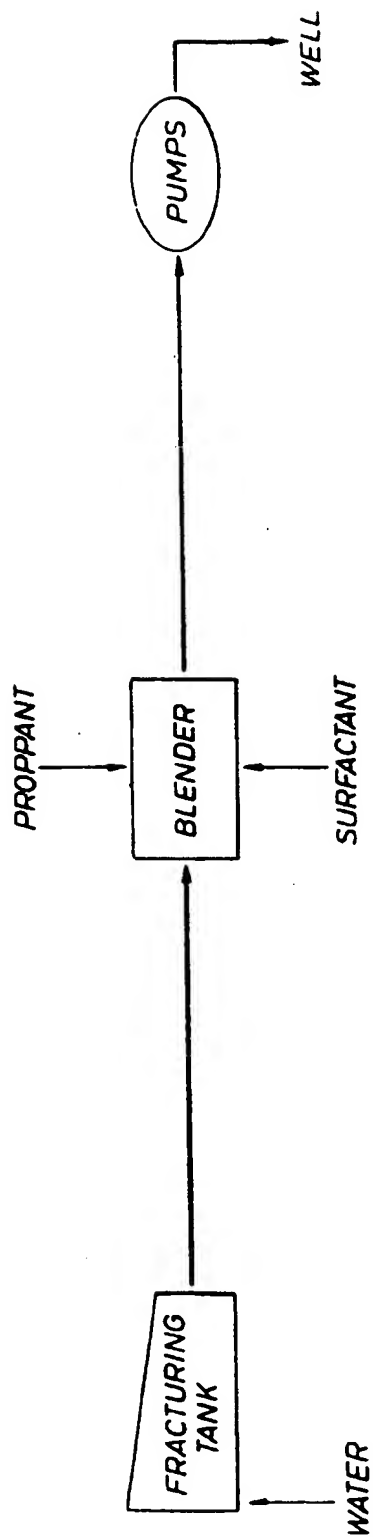


FIG. 4

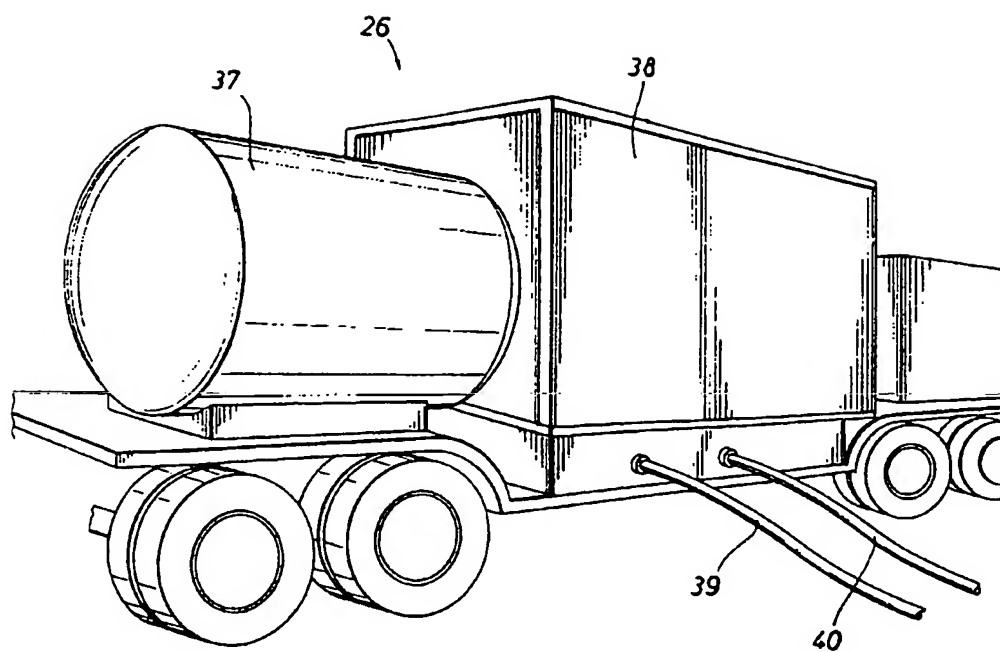


FIG. 2

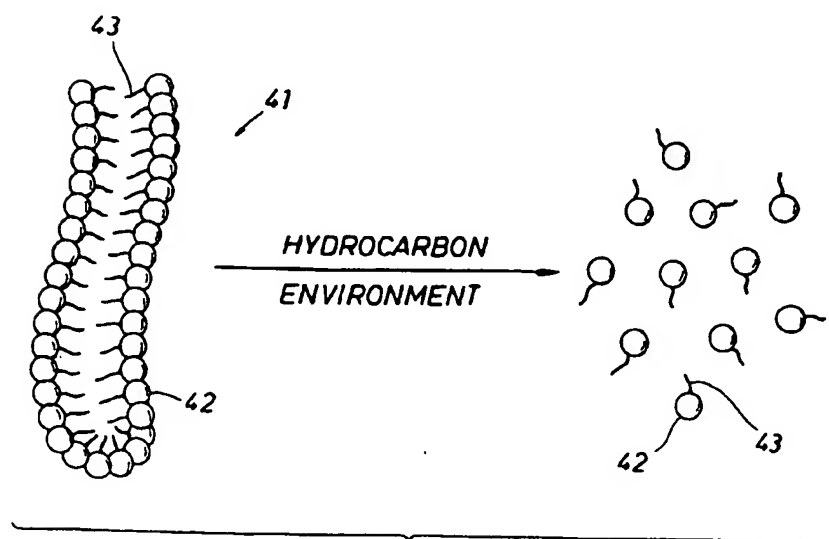


FIG. 5

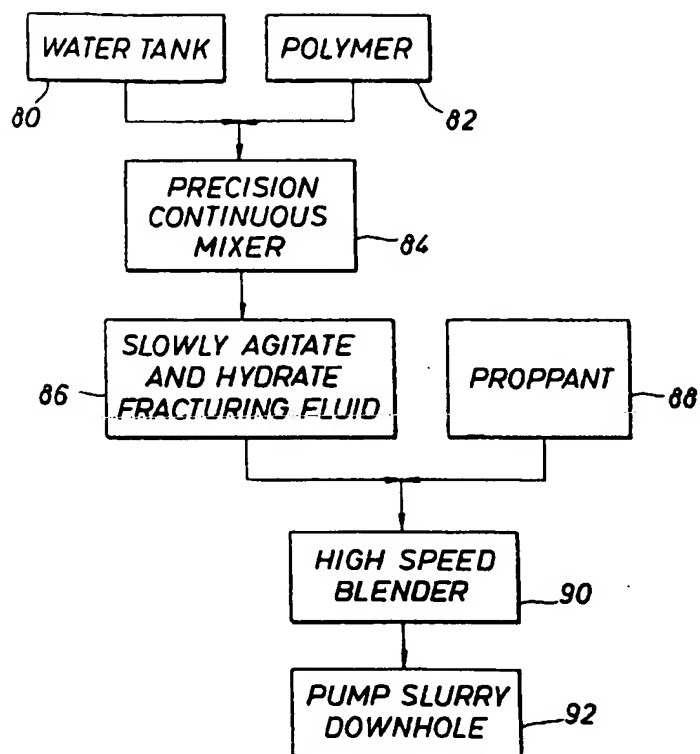


FIG. 3
(PRIOR ART)

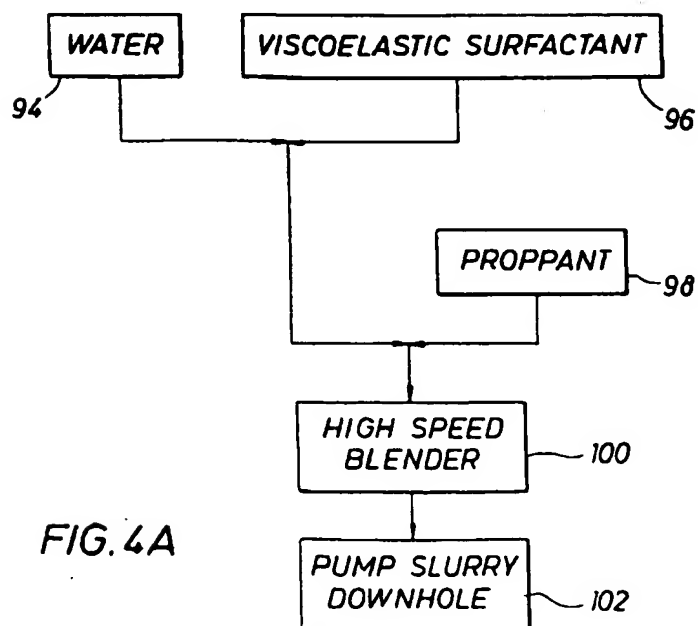
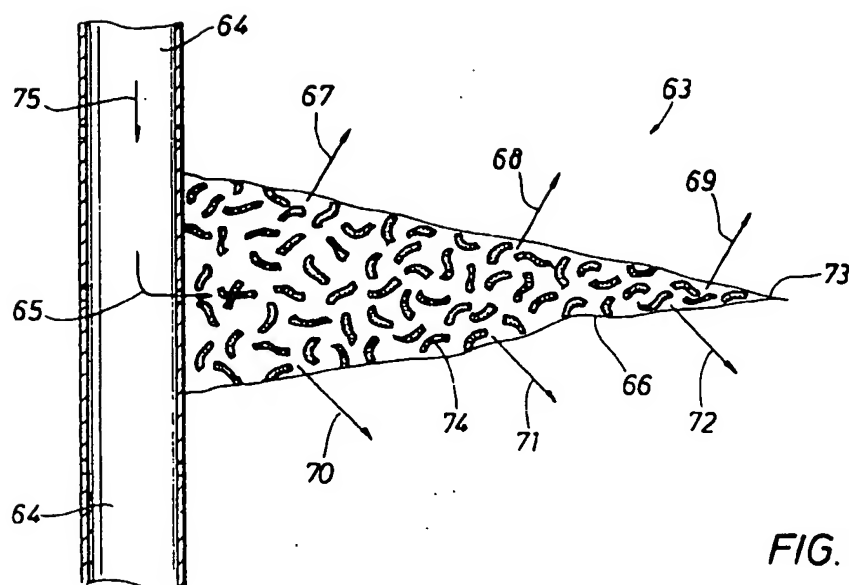
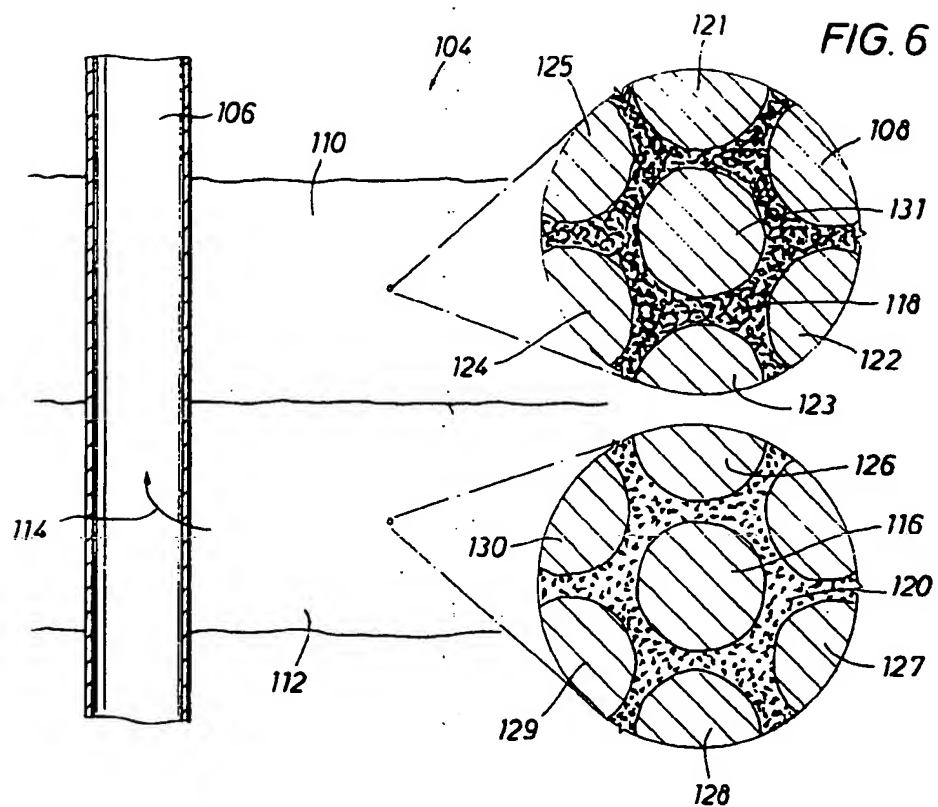


FIG. 4A



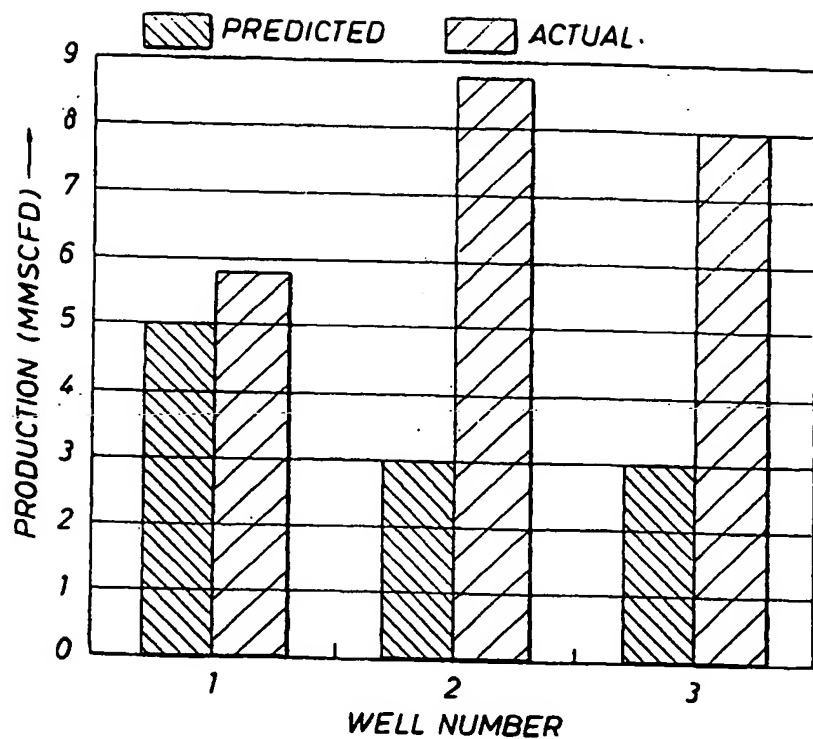


FIG. 8

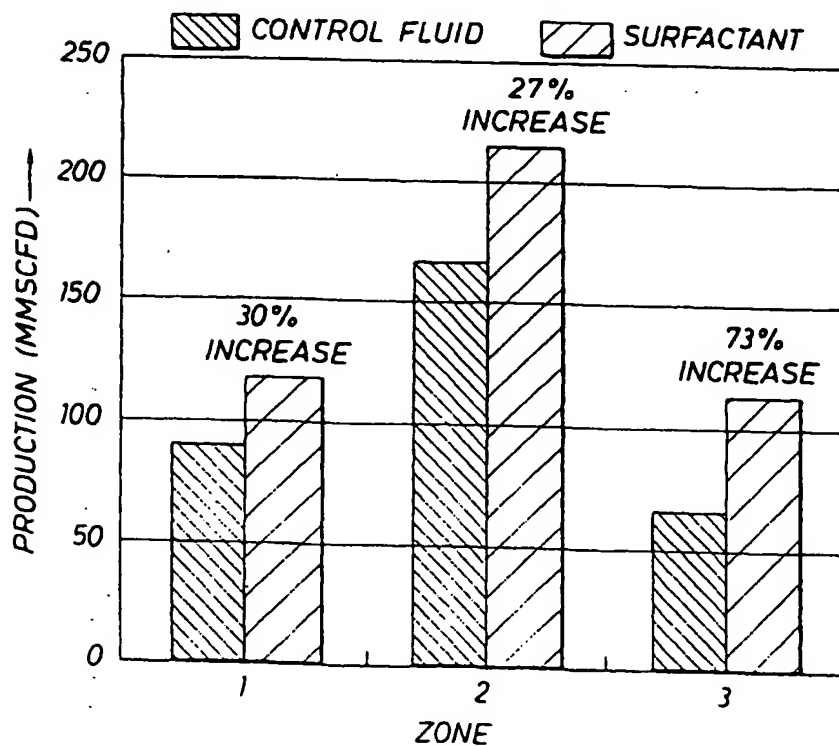
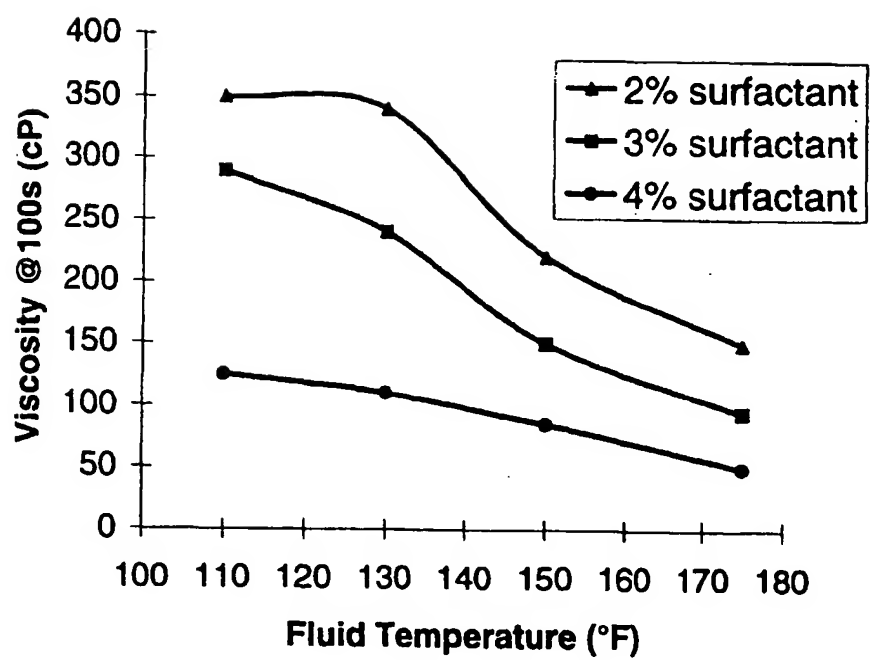


FIG. 9

**FIG. 10**